Limnologica 72 (2018) 1–9

Contents lists available at ScienceDirect

Limnologica

journal homepage: www.elsevier.com/locate/limno

Long-term change in the trophic status and mixing regime of a deep volcanic lake (Lake Bolsena, Central Italy)

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ARTICLE INFO

Keywords:
Eutrophication
Lake mixing
Climate change
Volcanic lakes

ABSTRACT

Lake Bolsena, the fourth Italian lake for volume (9.2×10^9 m^3), must be considered as highly sensitive to eutrophication for its extremely long water renewal time. In this paper, temperature and chemical characteristics of the lake measured in the period 2003–2017 are used to discuss the mixing pattern and the variation in the oxygen and algal nutrient concentrations, as indicators of the trophic level. In the analysed period the lake showed oligomictic characteristics, reaching the full overturn, with homogenization of the chemical profile over the whole water column, only in 4 out of the 15 considered years. A regular decrease of oxygen and increase of phosphorus concentrations in the deepest layers has been observed in the non-circulating multi-year periods. The mean total phosphorus concentration showed a regular increase, reaching values close to 16 µg P L^{-1} in early spring 2017, mostly because of the urban discharge from the watershed, not adequately collected from an existing sewage pipe. Chemical and mixing patterns are discussed in relation with a previous study, carried out in 1966–1971, confirming the recent increase of phosphorus concentrations and the lower frequency of full circulation. The progressive deterioration of lake water quality indicates the need of prompt actions to reduce the external nutrient load and of further studies on the physical and biological characteristics of the lake, still strongly missing.

1. Introduction

Lake Bolsena is the fourth largest Italian lake by water volume (9.2 km^3), following lakes Garda, Maggiore, and Como (49.0, 37.1, and 24.6 km^3 respectively). It is the most important water body of the Latium volcanic lake district, which includes lakes Bracciano, Albano, Vico, Nemi, and other smaller waterbodies, summing a total volume of 14.8 km^3 (Margaritora, 1992; Ambrosetti and Barbanti, 2002a,b; Fig. 1; Table 1). The Italian volcanic-lake system contains about 94% of the freshwater in central and southern Italy and 80% of the deep lakes within the Mediterranean coastal region (Azzella et al., 2014). These lakes altogether have a great importance in the economy of the area, with a high demand of water from agriculture and other civil uses, including drinking supply.

Lake Bolsena has been recognized by the EU as a site of community importance, due to its high naturalistic value and its role in the maintenance of biological diversity.

Due to its morphometric and hydrological characteristics, Lake Bolsena must be considered as highly sensitive to eutrophication and water pollution in general: this is mainly due to its very long renewal time, caused by the small surface area of the watershed in relation to the lake volume. A further threat to the water quality of this lake comes from the impact of climate change on the lake mixing regime and consequently on its oxygen and nutrient status. Several studies have highlighted how an air temperature increase may affect circulation dynamics in lakes through the different warming of surface and deep water layers (e.g. Livingstone, 2008; Straile et al., 2003). While epilimnetic temperatures reflect warming trends in air temperature, hypolimnetic temperatures exhibit a much more complex behavior and may undergo warming or cooling trends. Vertically heterogeneous changes in water temperature affect the density gradient in the water column and consequently the intensity and duration of vertical mixing and stratification, thermal stability, and the thermocline (Gerten and Adrian, 2001). Nutrient and oxygen concentrations may in turn be affected by changes in the thermal structure of the lake (Jeppesen et al., 2010; Hanson et al., 2006). These effects may be exacerbated in lakes with a limited hydrological recharge and a long renewal time as in Lake Bolsena. For this reason, in addition to catchment loads, climate drivers should be taken into account in the evolution of lake trophic status.

Lake Bolsena has been considered in limnological studies since the

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https://doi.org/10.1016/j.limno.2018.07.002
Received 24 January 2018; Received in revised form 11 July 2018; Accepted 14 July 2018
Available online 07 August 2018

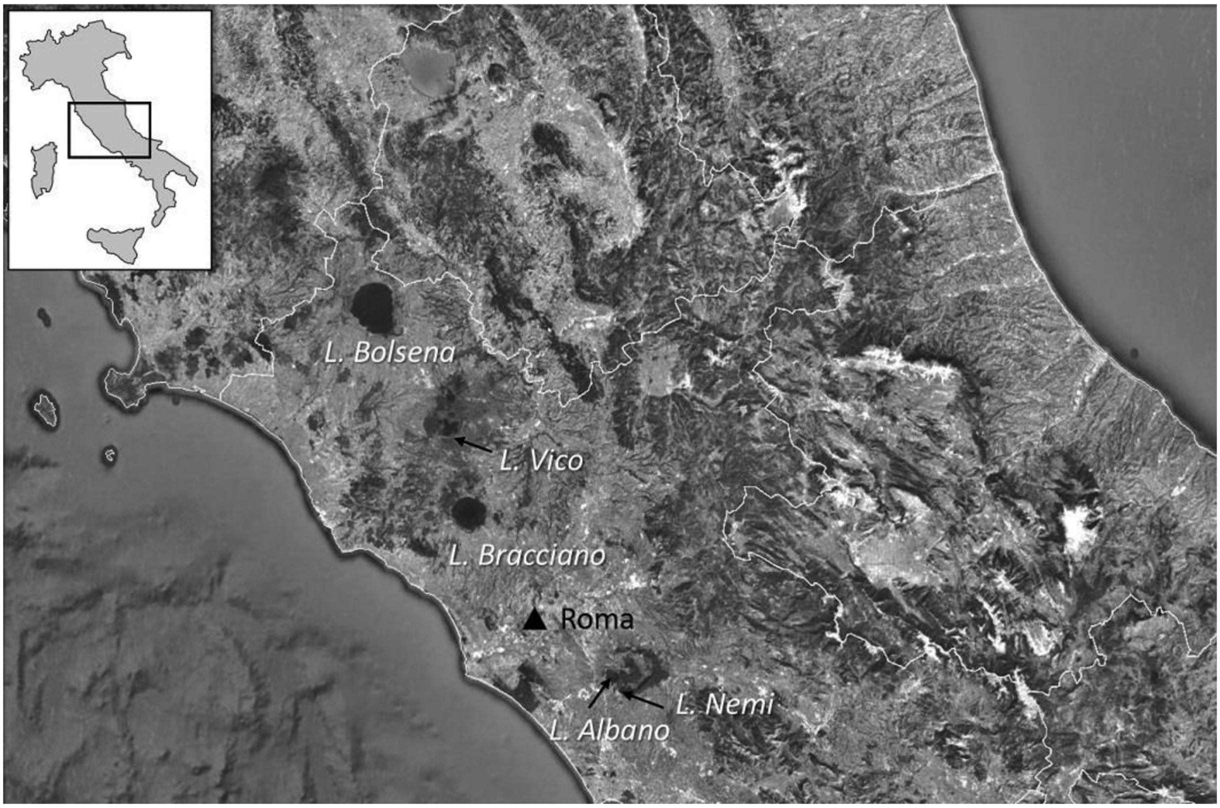

Fig. 1. Location of Lake Bolsena in the Latium lake district, Central Italy.

Table 1
Main morphometric and hydrological characteristics of Lake Bolsena.

Latitude N		42° 35′
Longitude E		11° 56′
Water level	m a.s.l.	304
Watershed max altitude	m a.s.l.	690
Watershed median altitude	m a.s.l.	490
Lake area	km^2	113.6
Watershed area (lake excluded)	km^2	159.4
Hydrogeological basin	km^2	342
Shoreline	km	43.2
Max. depth	m	151
Mean depth	m	81
Volume	km^3	9.2
Outflow discharge	$m^3 s^{-1}$	0.9
Theoretical water retention time	y	300
Precipitation	mm y^{-1}	980

end of the 19th century, when a bathymetric map and monthly measurements of temperature were performed from July 1896 to June 1897 (Gunther, 1904). More recent limnological studies were carried out after the 1950, mostly considering limited physical or biological aspects (for a review refer to Margaritora, 1992; Margaritora et al., 2003). The first detailed limnological study was carried out between 1966 and 1971 considering, besides Lake Bolsena, lakes Bracciano, Trasimeno, and Vico, aimed at the evaluation of the ecological impact on these lakes of a severe water diversion, planned for the production of electricity (Istituto Italiano Idrobiologia, 1971). The study included a new bathymetric map, and considered meteorological, hydrological, physical, chemical, and biological features (Gerletti, 1967; Gerletti and Melchiorri-Santolini, 1968; Ferrari, 1972).

A systematic study on thermal structure and water chemistry of the lake was performed between 1999–2001, in the framework of a collaboration between the Lake Bolsena Volunteer Association and the CNR Institute of Ecosystem Study (CNR-ISE), with purposes of both limnological study and environmental education. Regular limnological campaigns were then established, to assess in details the thermal and chemical properties of Lake Bolsena, compared with other lakes of the Latium district (Mosello et al., 2004). Yearly reports with results of the monitoring have been regularly published (e.g. Bruni, 2018). In this paper we aim to analyze the existing information, focusing on the recent evolution of Lake Bolsena (2003–2017) in relation to two main critical issues: (i) the trophic status, which has deteriorated with respect to the original oligotrophic condition, due to wastewater input and agricultural activities in the lake catchment; (ii) the thermal and mixing regime of the lake and its change over time. To this aim, long-term trends and seasonal patterns of nutrients and the main chemical variables related to the trophic state were assessed, with particular attention focusing on phosphorus and dissolved oxygen concentrations. The frequency and extension of mixing events at winter overturns were also assessed, in relation to meteorological variables. We formed the hypothesis that the air temperature increase registered in the lake area (Brunetti et al., 2006; Simolo et al., 2010) caused a decreasing frequency of full mixing events, with consequences on deep-water oxygen, nutrient concentrations and the lake water quality as a whole. We also discussed the possible role of hydrological change, in particular of increasing water withdrawal for several purposes, in the deterioration of lake water quality.

2. Methods

2.1. Study site

The origin of the lakes in the Latium district is mainly linked to Pleistocene volcanic activity and tectonic processes; in particular, the basins of Lake Bolsena and of the near Lake Bracciano were affected by recent regional tectonic activity and do not represent typical caldera lakes (Niessen et al., 1993). The volcanic origin of Lake Bolsena determined a total watershed surface of 273.1 km^2, including the lake

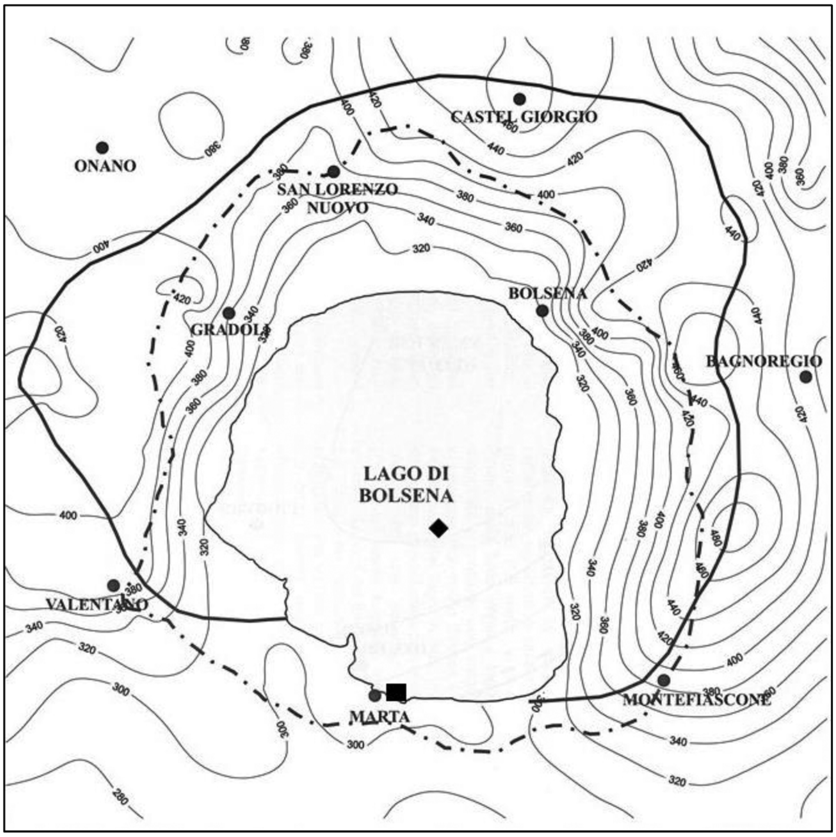

Fig. 2. Lake Bolsena, hydrographic (broken line) and hydrogeological (full line) basins (from Pagano et al., 2000). ◆ location of the sampling point. ■ location of the meteorological station in Marta.

surface (113.6 km^2; Table 1 and Fig. 2), a key aspect of critical concern in relation to the huge lake volume is the theoretical water renewal time which has been evaluated as 300 years (Ambrosetti et al., 2003). The topographic hydrogeological basin (350 km^2) is slightly larger than the phreatic watershed area (Bruni, 2018, Fig. 2). The water level is regulated at the outflow, in the village of Marta, where a small stream is formed, draining directly into the Tyrrhenian Sea.

The geology of the district is complex, with outcrops of very different rocks from the petrographical and granulometric points of view. The complex of vulcanites containing the lake has good porosity owing to the incoherent pyroclastic rocks and the fissuring of the lava and ignimbritic flows. This gives rise to a volcanic aquifer, supported by a clayey or flyschioid sedimentary substrate, of which Lake Bolsena represents the outcropping part (Bruni, 2018).

About 30,000 inhabitants live in the watershed of Lake Bolsena, whose beauty and location, not far from the city of Rome, lead to a significant touristic presence, enhancing the human pressure on the lake. Agriculture, together with professional and sport fisheries constitute further relevant economic resources.

Sewage reaching the lake was untreated until 1996, when a pipeline was constructed to convey wastewaters from the main inhabited centers to a treatment plant located about 3 km from the lake, along the outflow (Bruni, 2018). The pipeline does not serve the western shore of the lake, where the main camping and tourist facilities are present. Connections of the inhabited sewage systems to the pipeline are cared for by the different municipalities, and the transport is done through 20 lifting pumps. Further sources of pollution are agricultural runoff derived from cultures of potato and hazel grove. Lake water is used for these cultures and for the irrigation of meadow and vegetal gardens. In summer months, the amount of water used is around 15×10^6 m^3, about 50% of the total annual water usage (Bruni, 2018).

The area of Lake Bolsena and its islands are classified by the European Union as Site of Community Importance (cod. IT6010007, Habitats Directive) and Special Areas of Conservations (cod. IT6010055, Birds Directive) in the Natura 2000 network (Lynx Natura e Ambiente Srl, 2009).

2.2. Sampling and analytical methods

Chemical analyses were performed on samples collected twice per year (in February-March and November-December) at the depths of 0.5, 20, 30, 50, 100, 115 and 130 m. Samples were analysed at the water chemistry laboratory of CNR Institute of Ecosystem Study for the following variables: pH, conductivity, alkalinity (potentiometric methods), major anions (sulphate, nitrate, chloride) and cations (calcium, magnesium, sodium, potassium) (ion chromatography), ammonium, reactive phosphorus (RP) and reactive silica (RSi, spectrophotometry) total nitrogen and total phosphorus (TN, TP, spectrophotometry after oxidative digestion, Valderrama, 1981), and trace metals (ICP-OES). Organic nitrogen concentrations were obtained as difference between TN and ammonium + nitrate nitrogen.

Details on the analytical methods and the quality assurance/quality control program of the laboratory are provided at http://www.idrolab.ise.cnr.it/en, where the comparability of chemical data produced in the present (2002–2017) and previous studies (Gerletti, 1967; Istituto Italiano Idrobiologia, 1971) is discussed. The main difference concerns the sensitivities of RP (10 and 3 µg P L^{-1} for 1966-71 and 2003–2017 respectively). This bias does not permit a quantitative comparison of the concentration in the two periods for concentrations below 10 µg P L^{-1}.

Mean concentrations of the chemical variables in the epilimnion (0–25 m), hypolimnion (25–143 m), and between 100 m and the bottom were calculated as follows:

$\Sigma(Ci * Vi)/ \Sigma Vi$

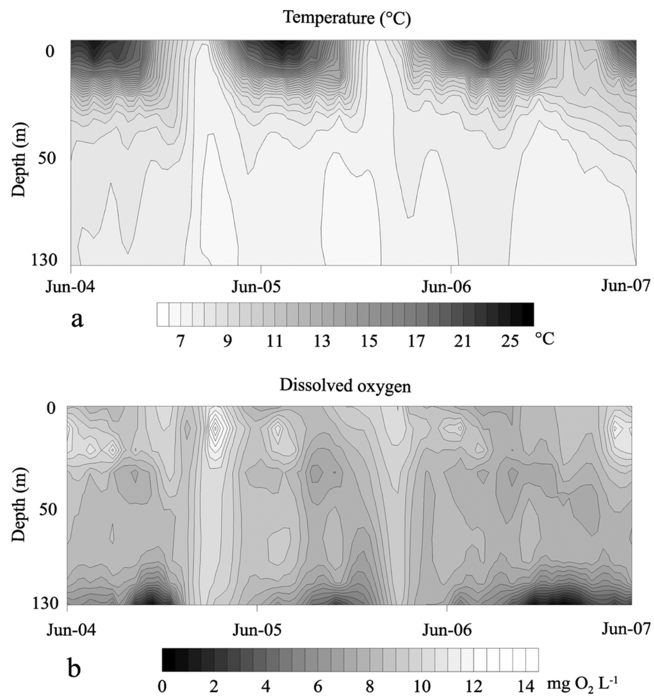

Fig. 3. Vertical distribution of temperature (a) and dissolved oxygen (b) in the water column of Lake Bolsena in the period June 2004–June 2007.

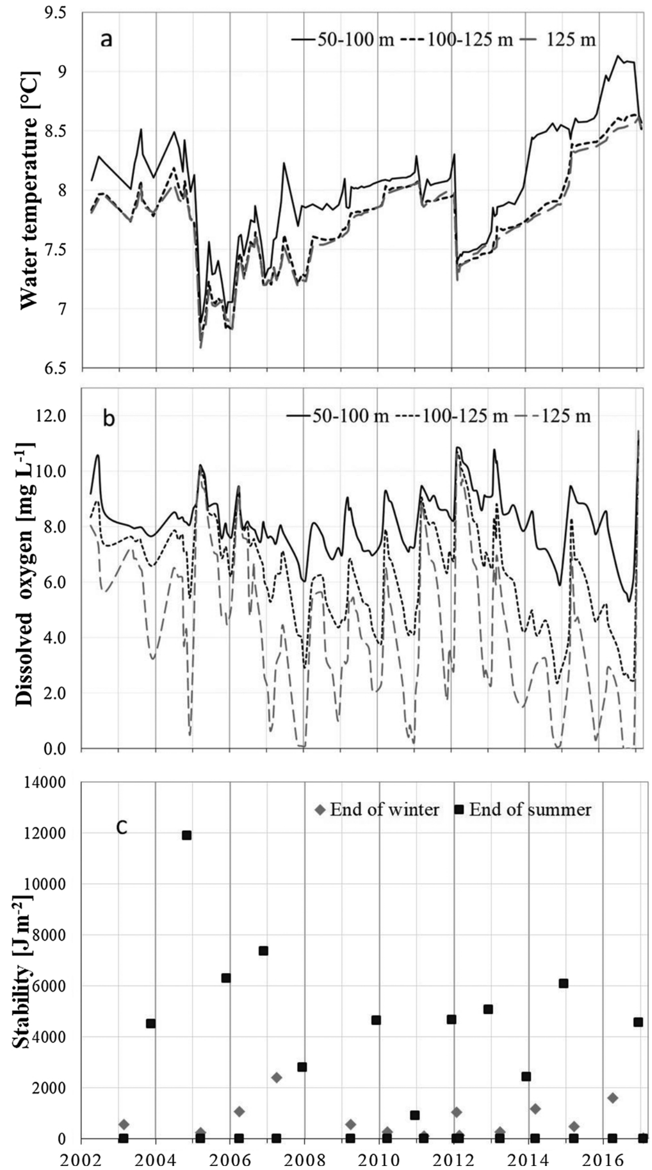

Fig. 4. Mean values of temperature (a) and dissolved oxygen (b) in different water layers of Lake Bolsena and Schmidt Stability of the water column (c).

where (Ci) is the concentration measured at depth i and Vi is the volume of the water layer attributed to depth i, calculated from the hypsographic curve of the lake.

Daily data of air temperature and wind speed for the period November 2009 – February 2017 were collected at the station of Marta, near the outflow of the lake (Fig. 2) and downloaded from http://www.meteomarta.it. Meteorological data are also available from the station of Acquapendente, located at about 12 km from Lake Bolsena (Mosello et al., 2004).

The Lake Analyzer v3.3.1 tool for limnological analysis (Read et al., 2011) was used to evaluate the thermal stability according to Schmidt (1928) and Idso (1973), defined as the work required to mix a thermally stratified lake in order to reach isothermic conditions under adiabatic conditions. The equation used for Schmidt Stability is (Read and Muraoka, 2011):

$$S_T = \frac{g}{A_s}\cdot\int_0^{z_d}(z-z_v)\cdot\rho_z\cdot A_z\partial z \quad [\mathrm{Jm^{-2}}] \tag{1}$$

where g is the acceleration due to gravity, A_s is the surface area of the lake, A_z is the area of the lake at depth z, z_d is the maximum depth of the lake, and z_v is the depth of the centre of volume of the lake, written as:

$$z_v = \frac{\int_0^{z_d} z\cdot A_z\partial z}{\int_0^{z_d} A_z\partial z} \tag{2}$$

3. Results and discussion

3.1. Thermal properties and mixing regime of the lake

The vertical distribution of temperature and dissolved oxygen (DO) in Lake Bolsena were assessed in detail in the period 2004–2007, when more frequent profile data were available (Fig. 3). Trends of temperature and DO are shown in Fig. 4a and b for different water layers. The complete datasets of temperature and oxygen profiles are shown in Tabb. 1S, 2S.

Surface water temperature ranged between 25–26 °C (July–August) and 7–8 °C (January-February). Water stratification started in April and persisted until December, with thermocline depth between 15–20 m in July-August, deepening to 25–30 m in October-November (Fig. 3a). The water column shows the highest thermal homogeneity in February-March, although a complete homeothermy was observed only in the springs of 2005, 2006, 2012, and 2017 (Figs. 3a and 4 a), when water temperature in the deepest layers suddenly decreased. Data of DO confirmed the occurrence of full mixing events: indeed, concentrations were close or above 10 mg O_2 L^{-1} and uniform throughout the whole water column in March of these years (Figs. 3b and 4 b).

Temperature and salinity data along the water column were used to evaluate the Schmidt stability for the whole lake (Fig. 4c). Values at the end of the winter period were much lower than those at the end of the stratification period, indicating that in the former condition a great amount of physical work is required to get a complete overturn. In the case of Lake Bolsena, this work is mostly related to wind, since the overturn due to water inflows (with cold and dense water entering in the deepest layers and oxygenating the hypolimnion) is negligible, due

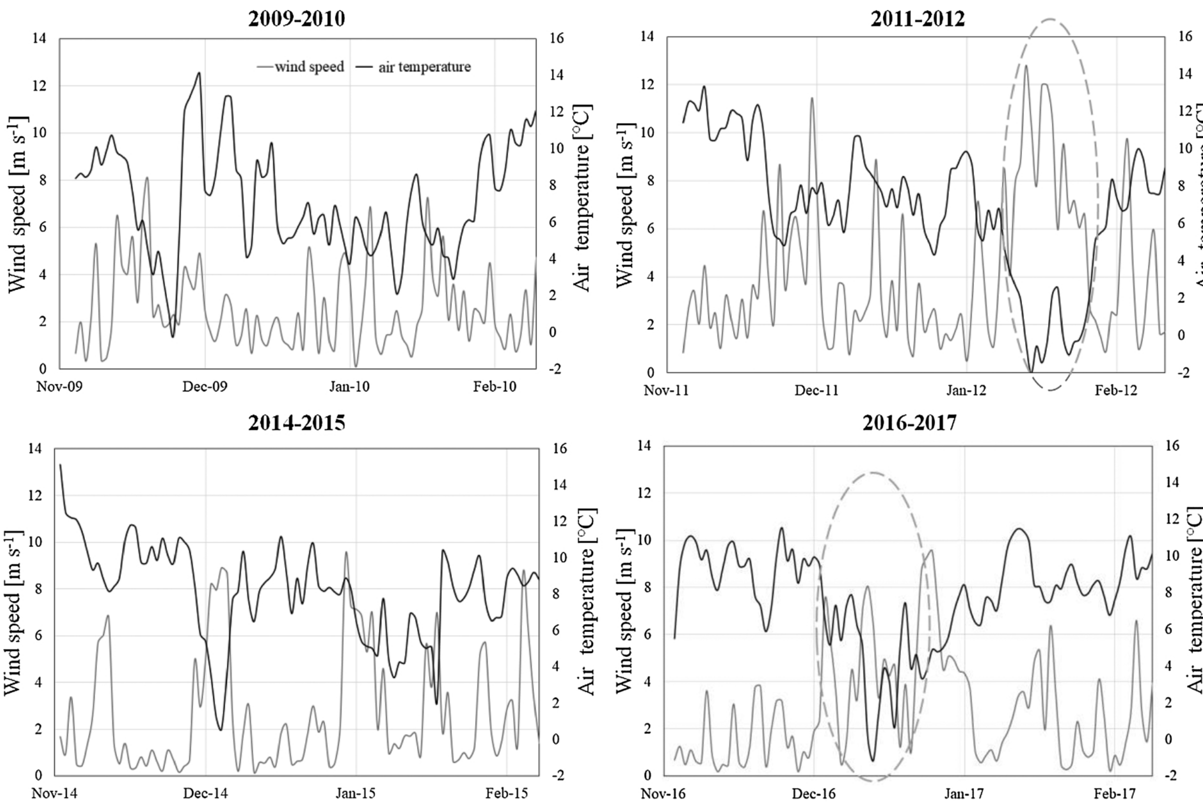

Fig. 5. Wind speed and air temperature in two winters without (left panels) and with (right panels) full overturns of the lake.

to the small hydrographic network in the catchment. The lowest value was recorded in January 2017 (19 J m^{-2}), followed by March 2011 (with 113 J m^{-2}), while the highest value of 2390 J m^{-2} was found at the end of winter 2007. The low temporal measurement resolution does not allow to exactly locate the local minimum in the Schmidt Stability values at the end of the winter. However, it is worth noting that in January 2017 a complete overturn took place, due not only to homoeothermic conditions, but also to the windy conditions of the first half of the month (see the remainder of this paragraph and Fig. 5). The value of 19 J m^{-2} suggests that the lake experienced full overturn shortly before or after the measurement was taken. On the contrary, a quite high value was found in March 2006 (1064 J m^{-2}); despite this, a full overturn took place in that period: this may depend on the fact that sampling was performed later than usual (end of March) and stratification had already started.

Overall, data showed that Lake Bolsena experienced full overturns only at the end of four limnological winters over a 16-year period (2002–2017). A comparison between the meteorological conditions (wind speed and air temperature) recorded in winters 2011–2012 and 2016–2017, when full overturns occurred, and those of 2009–2010 and 2014–2015, without full overturns, is shown in Fig. 5. Winter 2011–2012 was very cold, with a mean air temperature (December-February) of 6.84 °C, much lower than the winter mean for the period 2010–2017 (7.77 °C). In particular, air temperature reached very low values from the 1st to the 14th of February 2012, with an average of 0.38 °C (Fig. 5), much lower than the mean of February (7.56 °C). On the other hand, wind speed in winter 2011–2012 was higher both than the seasonal mean (2.57 m s^{-1}) and the mean of February (2.99 m s^{-1}), with a peak value of 8.46 m s^{-1} for the period from 1 st to the 14th of February 2012 (Fig. 5). In the same way, during the winter 2016–2017, seasonal mean air temperature was 7.73 °C, slightly lower than the winter mean for the whole period, while the average wind speed was 2.83 m s^{-1}, higher than the seasonal mean. In particular, in the period 5–20 t h of January, the mean air temperature was 3.48 °C and the mean wind speed was 5.56 m s^{-1}. It should be highlighted that both conditions (below- and above-average values for air temperature and wind speed, respectively) had to be present to foster the mixing of the lake. On the other hand, years without full overturn were characterised by winters in which neither air temperature nor wind speed reached very low or high values, respectively, for prolonged periods.

Studies carried out in the period 1966–1970 indicated that complete overturns of Lake Bolsena occurred in three out of four winters, in particular in 1966-67 (Gerletti, 1967), 1968–69 and 1969–70 (Istituto Italiano Idrobiologia, 1971). According to such information, it can be hypothesized that the mixing frequency of the lake is changing, with the lake behavior going from warm monomictic in the 1960s (full overturn occurring every year at the end of the limnological winter), to oligomictic in recent years (mixing occurring only at the end of particularly cold and windy winters). This tendency towards less frequent overturn has been reported both by modelling exercises and long-term data analysis for several lakes (e.g. Weinberger and Vetter, 2014; Sahoo et al., 2016) and related to climate warming and increasing stability of the water column (Straile et al., 2003). A recent study on Lake Garda, Northern Italy, yielded evidence of important ecological shifts in this large and deep lake as an effect of climate change (Salmaso et al., 2017): in particular, the lake underwent a strong decrease in the frequency of full mixing episodes and the beginning of a meromictic period since 2007. Similarly, the other deep lakes of the subalpine lake district in Italy (Lugano, Maggiore, Como, and Iseo) experienced a recent increase in water column stability and a decrease in mixing extent and frequency, with an overall effect on water quality (Rogora et al., 2018). Other studies on deep lakes north of the Alps showed that reduced water turnover may also favor harmful algal blooms (e.g. Posch et al., 2012), with undesired effects similar to those caused by cultural eutrophication.

In Lake Bolsena, these effects may be exacerbated by the limited water renewal. Indeed, besides the increasing stability of the water column, a critical issue in this lake is its very long renewal time. The

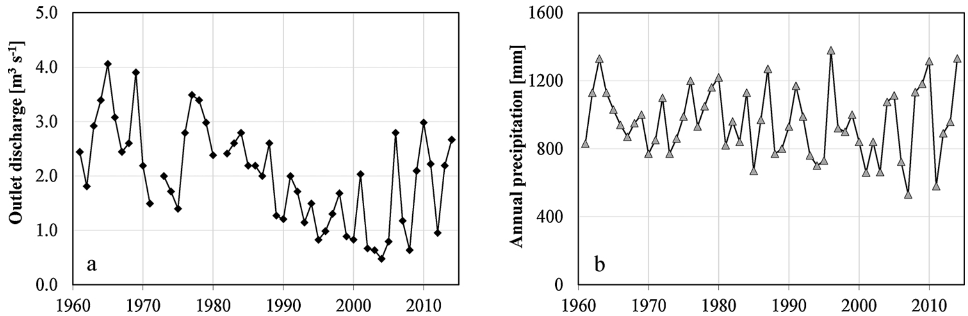

Fig. 6. Trends of average annual discharge of Lake Bolsena outlet (a) and annual precipitation amount measured in Acquapendente (b).

water level of the lake is regulated at the outflow, and data on both the lake level and the outlet discharge have been collected since the 1960s (Bruni, 2018). The average annual discharge of the outlet strongly decreased in the period 1960–2005, from a flow rate of 2.4 $m^3\ s^{-1}$ to 0.9 $m^3\ s^{-1}$, (Fig. 6a), increasing the water theoretical renewal time from 120 to more than 300 years (Ambrosetti et al., 2003). This variation is only partially due to the precipitation amount, which slightly decreased in the last 50 years (Fig. 6b), causing a negative water balance of about $10^6\ m^3\ y^{-1}$ (Pagano et al., 2000). The cause is mainly due to the continuous increase in water abstraction within the lake's catchment for drinking and irrigation purposes. As an example, it has been estimated that in the year 2000 the drilled wells numbered over 1000 and yielded $35 \times 10^6\ m^3\ y^{-1}$ (Pagano et al., 2000, Fig. 1S).

3.2. Water chemistry

3.2.1. Major ions and trace metals

The average ionic composition of Lake Bolsena waters, measured at winter overturn (Table 2), was characterised by high solute concentrations (10.8 meq L^{-1} as the sum of major ions). Bicarbonate, which in the pH range 7.9–8.5 is the prevailing form of inorganic carbon, represents 37.5% of the total ionic content, being the most important anion, followed by chloride (7.5%). Among cations, sodium showed the highest concentration (17.3%), followed by magnesium, potassium and calcium (respectively 12.1, 11.9 and 9.2%).

The concentrations of other solutes, measured at the winter overturn (Table 3), showed moderate values of strontium and boron, the latter being frequent in water bodies located in volcanic areas (Varekamp, 2015). The remaining trace elements such as barium, copper, iron, manganese, zinc and lithium were present in very low concentrations, in most cases close to the limit of detection (LOD) of the method used. Arsenic concentrations showed values below 5 µg L^{-1}, also close to the LOD.

Table 2
Ionic balance of Lake Bolsena waters (average values measured at winter overturn for the period 2014–2016) compared with the values of the period 1965–66 (Gerletti, 1967) and % difference between the two periods (Δ). Italic characters indicate the % contribution of each ion to the total ionic content.

	2014-16		1965-66		Δ (2016-1966)
	meq L^{-1}	%	meq L^{-1}	%	%
HCO_3^-	4.11	*37.5*	3.94	*37.5*	4.3
$SO_4^=$	0.41	*3.8*	0.47	*4.5*	−12.8
NO_3^-	0.008	*0.1*	0.010	*0.1*	−20.0
Cl^-	0.83	*7.5*	0.76	*7.2*	9.2
F^-	0.07	*0.7*	0.08	*0.8*	−12.5
Ca^{++}	1.01	*9.2*	1.08	*10.3*	−6.5
Mg^{++}	1.32	*12.1*	1.15	*11*	14.8
Na^+	1.9	*17.3*	1.8	*17.1*	5.6
K^+	1.3	*11.9*	1.2	*11.5*	7.4
Σ anions	5.43	*49.5*	5.26	*50.1*	–
Σ cations	5.53	*50.5*	5.24	*49.9*	–
Σ ions	10.96	–	10.5	–	4.4

Table 3
Mean concentrations of trace elements measured in Lake Bolsena in March 2014. Volume weighted mean on the water column; unit µg L^{-1}. LOD: limit of detection.

	0–25 m	25–130 m	100–130 m	LOD
Aluminum	3	3	3	3
Arsenic	3.4	4.7	3.3	4
Boron	580	594	600	10
Barium	36	36	36	0.4
Copper	1	1	1	0.8
Iron	2	2	2	1.5
Manganese	0.3	0.2	0.2	0.2
Lithium	32	32	32	3
Strontium	412	413	415	0.1
Zinc	5	8	11	0.5

Dissolved oxygen (DO) in the deep waters ranged between 4 and 6 mg L^{-1}, definitely lower than the values of the epilimnion and the 50–100 m water layer (Fig. 4b, Tab. 2S). The peak values in the epilimnion (11–12 mg L^{-1}) were reached in spring and summer, in relation to primary production, as confirmed also from the concomitant peak values of pH, ranging between 8.5 and 8.7, compared with mean values of 8.1–8.3 (Fig. 7a). Anoxic conditions were detected in the deepest 5 m water layer in the winter months in 2013, 2014, 2015 and 2016 (Fig. 4b).

Nitrate and organic nitrogen are the most important forms of nitrogen in lake waters, with mean values of 113 and 160 µg N L^{-1} respectively at winter overturn, accounting for 41 and 57% of the total nitrogen content. Nitrate always showed a relevant stratification over the water column, with the lowest values in the epilimnion (< 10 µg N L^{-1} in autumn) and the highest concentrations in the water layer at 100–130 m depth (about 200 µg N L^{-1}). Only during the four episodes of full overturn were nitrate concentrations uniform throughout the water column (about 100 µg N L^{-1}; Fig. 7b, Tab. 3S).

During the stratification periods, RP and TP values in the epilimnion were generally lower than 10 µg P L^{-1} due to algal uptake, increasing in the deepest layers, where phosphorus accumulates forming an important stock, which may be brought back to surface layers during mixing events (Fig. 7 c and d, Tab. 4S). Concentrations in the water layer below 100 m were higher than in the layers above, with marked seasonal variations in relation to the winter mixing of waters (Fig. 8). The highest concentrations were measured in December 2016 (42 and 55 µg P L^{-1}, Fig. 7c and d), and corresponded to the lowest DO concentration (mean 1.8 mg L^{-1} in the water layer 100–130 m and anoxia in the layer 120–130 m; Fig. 4b).

The seasonal variations of concentrations with depth at the end of the stratification period was negligible for Na^+, K^+, Mg^{++}, Cl^- and $SO_4^=$, while Ca^{++} and bicarbonate showed, if compared with spring values, lower concentration in the epilimnion and higher in the deep waters, likely due to the precipitation of $CaCO_3$ induced from photosynthetic processes (Fig. 7e and f). The variation of conductivity in the

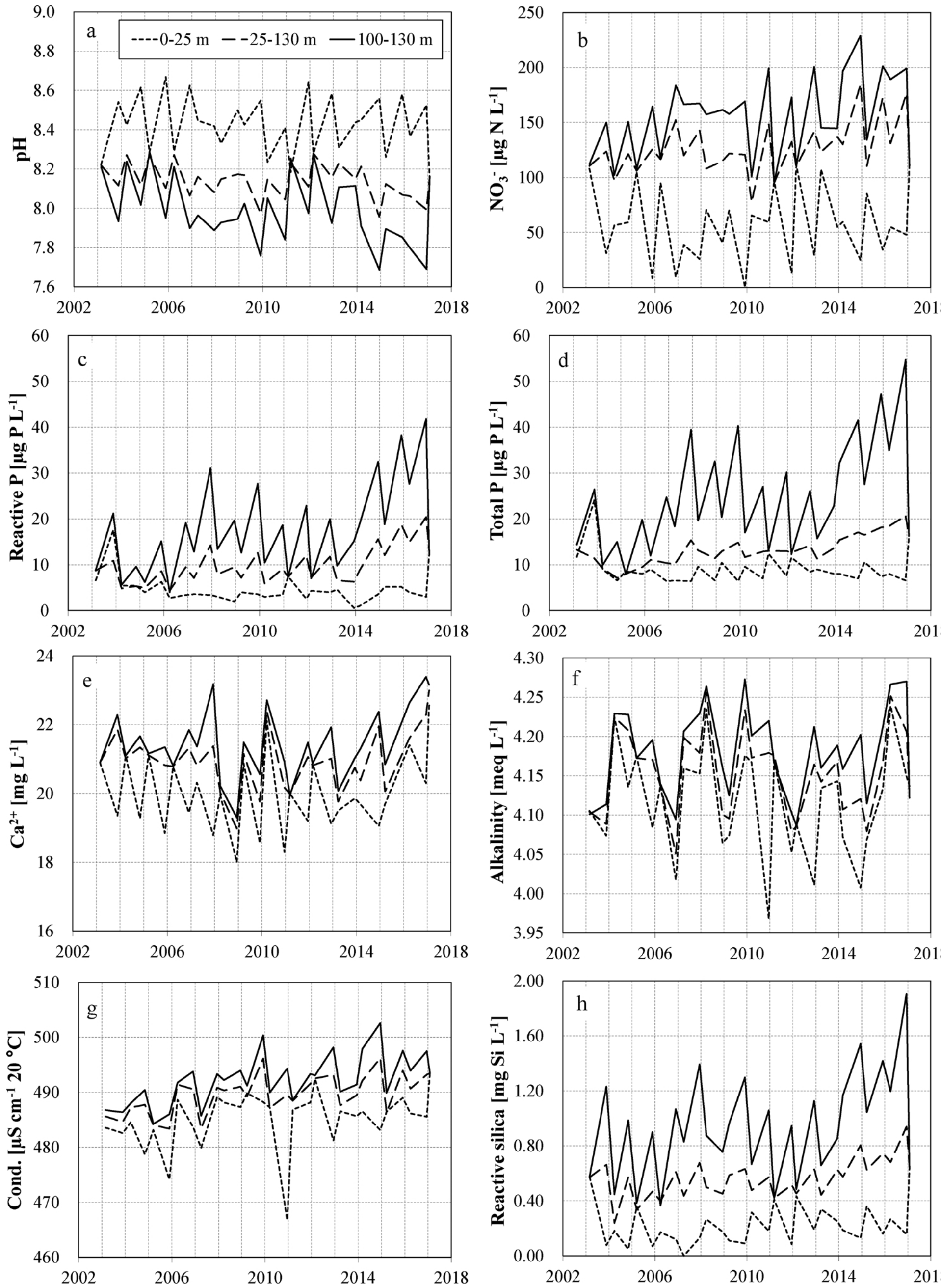

Fig. 7. Trends of selected chemical variables in different water layers of Lake Bolsena in the period 2003–2017. Two samplings per year, at overturn (February-March) and at the end of the stratification period (November-December).

two water layers is consistent with these values (483 and 498 µS cm^{-1}, respectively; Fig. 7g).

As regards the major ions, a comparison between the mean concentrations expressed as ionic balance measured in the recent period with those of the 1960s shows an increase of 4.4% of the total concentrations (Table 2). The most likely cause of ion increase is an enhanced weathering in the watershed and a decrease of water inflow to the lake.

3.2.2. Algal nutrient concentrations and trends

Total and reactive phosphorus are by far the chemical species showing the most important variation in the period of observation (Tabb. 4S and 5S). Mean lake concentrations measured at winter overturn increased from about 5 to 12 (RP) and from 9 to 16 (TP) µg L^{-1} respectively (Fig. 8). According to the Mann-Kendall test, the trend of TP concentrations measured at overturn was highly significant ($p < 0.001$); the average rate of increase, calculated according to Sen (1968), was 0.54 µg P L^{-1} y^{-1}, with an increase of 7.6 µg P L^{-1} over the period 2004–2017.

These data show that Lake Bolsena moved from oligotrophy in the early 2000s to the present mesotrophic state.

Also in the case of reactive silica, a slight increase of concentrations occurred in the study period, from average values of 0.44 mg L^{-1} in 2002–2005 to 0.55 mg L^{-1} in recent years, more evident in the deep water layer (Fig. 7h, Tab. 6S).

Nitrate concentrations, remained unchanged when considering the average values on the water column (Table 2). However, a slight

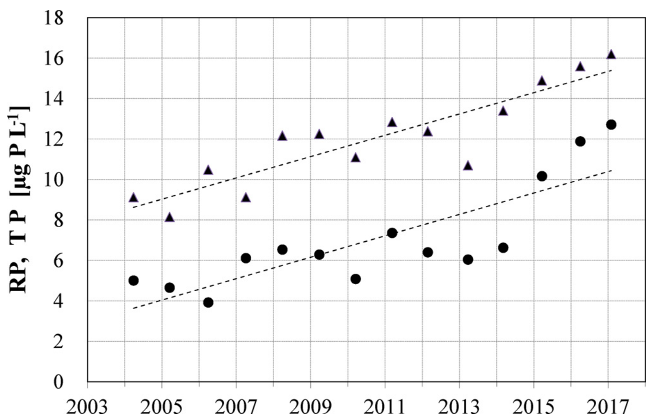

Fig. 8. Volume weighted concentrations of RP (dots) and TP (triangles) measured in Lake Bolsena at winter overturn in the period 2004-2017.

tendency towards higher nitrate concentrations in recent years can be seen in the hypolimnion of the lake: values around 150 and 200 µg N L^{-1} were measured in the layers 25–130 and 100–130 m, respectively, in the last few years (2014–2017), with respect to 125 and 155 µg N L^{-1} in the previous period (Fig. 7b). As for TP and RSi, this accumulation of nitrate in the deep waters, more evident since 2013–2014, is an effect of the lack of complete overturn of the lake for some consecutive years: nutrients are progressively stored in the hypolimnion but are then released during the following mixing events, with potential eutrophying effects on the surface water layers.

RP concentrations at overturn showed mean values always lower than 10 µg P L^{-1} in the 1960′s, while this threshold was exceeded in all the samplings after 2013, reaching the concentrations of 13 µg P L^{-1} at the 2017 overturn (Fig. 8).

These data confirm the progressive accumulation of phosphorous in Lake Bolsena, due to an increase in the external load and accentuated by the long renewal time of the lake: phosphorous indeed remains in the lake, both increasing the concentration in the waters and accumulating in the sediments. A seasonal P release from sediments appears unlikely in current oxygenation conditions as, although the complete absence of oxygen has been monitored, nitrate remains present in solution, to sustain microbial respiration other than Fe reduction (Hupfer and Lewandowski, 2008). However, trend toward anoxia is further amplified by the predicted global warming, which reduces the frequency of complete seasonal deep mixing compared to the present situation, aspects documented in this paper for Lake Bolsena. The increase of water temperature, at the same P load, enhance algal productivity and, consequently, sediment flux and mineralization in the hypolimnion (Matzinger et al., 2006). A detailed study performed on Lake Ohrid demonstrated the need of a reduction of P load of 50% to compensate the effect of global warming on algal productivity in the next decades (Matzinger et al., 2007).

Possible malfunction of the sewage pipe infrastructure and loss to the lake through spillways during heavy rainfall should be of particular concern and remedial action adopted. The sewage system of the served municipalities also collects runoff, thereby contributing to a further decrease of water input to the lake. Phosphorous and nitrogen are also used as fertilizers for potato and hazel grove, which require underground water for irrigation (Mosello et al., 2004; Bruni, 2018).

Lack of funding did not allow an update of biological data; those available for the period 1966–1971 confirmed the oligotrophic condition of the lake at that time (Istituto Italiano Idrobiologia, 1971). However, an indication on the trophic evolution of the lake, updated to 1993, comes from a palaeolimnological study, considering organic matter, calcium carbonate, biogenic silica, carbon, nitrogen and algal pigments, which shows a significant increase of the concentrations in the upper sediment layer (Massaferro et al., 1994).

4. Conclusions

Lake Bolsena and its watershed constitute an environment of extraordinary importance and beauty, fully justifying the designation of this site as being of European interest. Unfortunately, some aspects make it sensitive to eutrophication, such as the very high water renewal time making it a sort of closed lake, and a mild climate that, together with the lake's specific depth and volume, determine oligomictic characteristics, with incomplete water mixing for several years. These features altogether emphasize the sensitivity of the lake to external nutrient loads. In fact, although the present chemical data of Lake Bolsena still indicates mesotrophic condition, this study clearly shows an ongoing increase in the trophic level and the need for prompt actions. The first and most important signal is the increase of RP and TP concentrations: the causes are likely to be the P load from the catchment, coming from urban sewage, not completely collected from the sewage ring, and agricultural fertilizer.

The effects of the increased trophic level are evident in the seasonal variations and through the vertical profile of the chemical variables, in particular those affected by biological processes (dissolved oxygen, nitrate, phosphorous and reactive silica).

A further factor influencing the oxygen concentration in the deep waters is the decreased frequency of mixing events, in turn affected by climate change. Anoxic conditions of bottom waters are already occurring, although for short periods, and may produce a release of P from the sediments with the formation of an internal P load, in addition to the external one.

The sensitivity of the lake towards eutrophication and water pollution in general is enhanced by its very slow water recharge; this has been further reduced in time by decreasing the water outflowing from the lake by more and more consistent water withdrawal for various purposes.

The recent evolution of the lake prompts the need for interventions, which must be directed both to reduce the external phosphorus loads and to limit or regulate the water withdrawal from the aquifer of the lake. In lakes of such large volume and depth as Lake Bolsena, modifications of water quality are relatively slow, but an even longer time will be needed to recover the lake's natural oligotrophic condition. Lake Bolsena, due to its high nature value which fundamentally underpins the economy and wellbeing of the area, is worthy of greater attention from the responsible authorities and from citizens.

Acknowledgments

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. We thank Mr. Luca Viviani, in charge of the meteorological station in Marta (VT), which provided meteorological data. Thanks are due to A. Marchetto and D. Fontaneto of CNR ISE for their suggestions, to R. Caroni for the language editing and to two anonymous referees for their valuable comments over the manuscript. We acknowledge the activity of the staff of the chemical laboratory at CNR Institute of Ecosystem Study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.limno.2018.07.002.

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